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Thermochemistry and Kinetics of Sulfur Containing Molecules and Radicals

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Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

Nov 77

EPA-600/3-77-127
November 1977

PB 275 721

Ecological Research Series

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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-77-127		PB275721

4. TITLE AND SUBTITLE	5. REPORT DATE
THERMOCHEMISTRY AND KINETICS OF SULFUR CONTAINING MOLECULES AND RADICALS	November 1977
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Sidney W. Benson	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
University of Southern California Los Angeles, California 90007	1AA603
	11. CONTRACT/GRANT NO.
	DA-6998290
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Final
	14. SPONSORING AGENCY CODE
	EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Sulfur inorganic compounds * Sulfur organic compounds * Thermochemistry * Reaction kinetics		13B 07B 07C 07D

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	58
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE PC A04 / MF A01

EPA Form 2220-1 (9-73)

EPA-600/3-77-127
November 1977

THERMOCHEMISTRY AND KINETICS OF SULFUR CONTAINING MOLECULES AND RADICALS

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SECTION 1

INTRODUCTION

Sulfur is one of the abundant elements in the earth's crust. It is important in industry, in agriculture, in biology, and in air pollution. Because it occurs in crude oil to the extent of 0.2 to 5.0% and in coals in the range of 0.2 to 10%, a great deal of research work has been directed to develop processes for the desulfurization of coal, oil, and fuels generally. An almost equal amount of work has been directed towards the removal of sulfur-containing species from the exhaust stacks of power plants and factories (1). The increasing stringency of air quality standards has required a more sophisticated understanding of the chemistry and kinetics of sulfur-containing species, particularly at low concentrations. This has accelerated efforts to model the combustion and oxidation of sulfur compounds as a means to better control both the production and the eventual removal of sulfur oxides (2). Comparable efforts have been made to understand the detailed molecular steps whereby sulfur oxides in the ambient atmosphere become converted to sulfuric acid and visibility-reducing aerosol particles (3).

One of the basic requirements in such modeling efforts is detailed knowledge of the thermochemistry of the molecular and radical species involved in these steps. Such information is of importance both in interpreting some of the complex kinetic systems that have been studied and also in simplifying the oppressively large sequence of possible kinetic steps that may be significant in the molecular pathways for the overall reactions.

This report will present a review of the relevant thermochemistry and select "best" values for use in analyzing the kinetic systems. Although the kinetics of air pollution and combustion involve mostly homogeneous gas phase reactions, the data taken from condensed phases will be included because of their great utility. All of the available thermochemistry on organic and relevant inorganic sulfur-containing molecules and radicals through 1976 will

be reviewed, then more briefly the significant or controversial kinetic steps of importance in air pollution and combustion.

The task in both these areas is enormously simplified by the availability of a number of recent surveys. Authoritative compilations of the thermochemistry of sulfur-containing molecules have been made by Cox and Pilcher (4) and by Stull, Westrum, and Sinke (5). Perhaps the most detailed and critical evaluation on selected compounds comes from the JANAF series (6). Extensive use will be made of the NBS series of "Selected Values of Chemical Thermodynamic Properties", Tech. Note 270-3 (7), a valuable supplement to the preceding surveys,particularly for inorganic compounds. Unfortunately, since it is neither documented nor critical, the original literature sources have been reviewed where possible. A critical survey of the thermochemical data on gas phase organic species containing sulfur, published by the author and colleagues (8), will be used particularly for data on S^{o} and Cp^{o} and the methodology of group additivity.

Much less information exists on the heats of formation of sulfur-containing radicals. Mackle (9) made the first extensive survey of bond strengths in organic sulfur molecules, and some of these were included by Kerr (10) in his review of bond energies obtained by kinetic studies. Many were omitted by Kerr because of the "speculative" nature of the initial evidence. Much of this work and subsequent data have been discussed and reevaluated by Benson and O'Neal in their monograph on unimolecular reactions (11). Some of this work has been in turn updated in a recent review (12). This report will also make use of kinetic data obtained from studies in condensed phases. Empirical rules can be employed to translate this data to equivalent gas phase species, albeit with some uncertainty.

The format will present and discuss the thermochemistry of divalent, then tetravalent, and finally hexavalent sulfur compounds. The relevant bond strengths will be treated in each appropriate section together with the radicals involved. The last section will treat the kinetics of oxidation processes. In what follows all energies will be expressed in kcal/mole, while Cp^{o} and S^{o} will be in cal/mole-^{o}K (e.u.). A large number, but not all of the sulfur-containing compounds will be included in the tables. The omitted species may be found in one or more of the sources quoted, or their thermochemical properties may be

deduced by methods of group additivity from published tables (13). Table 1 lists all the revised group estimates and new groups obtained in the present work.

TABLE 1. SOME REVISED AND NEW GROUP VALUES FOR USE IN GROUP ADDITIVITY ESTIMATES

Group	ΔH°_{f298}	Group	ΔH°_{f298}
$S-(C_d)_2$	13.5	$O-(H)(SO_2)$	-38.0*
$S-(C)(C_d)$	13.0	O-(H)(S)	-38.0*
$S-(H)(C_d)$	6.1	O-(H)(SO)	-38.0*
$S-(S)_2$	3.2	$O-(SO_2)_2$	-4
$S-(O)_2$	+9 ±4	$O-(O)(SO_2)$	3
		Ring Corrections	ΔH°_{f298}
$SO-(O)_2$	-51 ±3	Thiophene	-16.3
$SO_2-(O)_2$	-101	Thiacyclopentene-2	2.0
$SO_2-(F)(O)$	-142	cyclo-S_3	22.9
$SO_2-(Cl)(O)$	- 97	cyclo-S_4	18.4
		cyclo-S_6	5.3
		cyclo-S_8	-1.1

* These are assigned values in accord with usual conventions.

SECTION 2

THERMOCHEMISTRY OF DIVALENT SULFUR COMPOUNDS

The thermochemistry of divalent sulfur compounds seems to be fairly well established, very little new work having been done since the previous reviews (4,5,8). Consequently, these values will be used in the discussions. The thermochemistry of the organic divalent sulfur compounds seems not only reliable but also self-consistent in that it seems to follow empirical rules of group additivity (8) quite well. This is of considerable help since it means that group additivity rules can be employed with confidence to deduce the thermochemistry of species whose values have not been explicitly measured. The one exception to this rule seems to be the derivatives of ethylene sulfide, where the apparent strain energy seems to depend on the amount of ring substitution (8). Consequently, these values may be considered uncertain to about $\pm$ 2 kcal despite the good calorimetric precision in measuring their heats of combustion.

The group values used to estimate the thermochemistry of compounds not given here have recently been republished (13), but some corrections based on recent studies are in order. The changes are as follows:

For the S-(C)(C_d) group, the value ΔH°_{f298} = 13.0 kcal instead of the original 10.0 kcal will be used. For the related group S-(H)(C_d), based on various analogies, the value ΔH°_{f298} = 6.1 kcal has been derived. For the S-$(S)_2$ group, ΔH°_{f298} = 3.2 kcal (instead of 3.0) will be used. For thiacyclopentene-2 a strain energy of 2.0 kcal, has been assigned rather than the value of 5.0 kcal, while for thiophene the value is not separable from the value of the group S-$(C_d)_2$. If ΔH°_f is assigned for the latter as ΔH°_{f298} = 13.5 kcal, rather than the -4.5 kcal originally assigned, to make for a more reasonable behavior of open chain compounds, then it leads to a strain energy in thiophene of -16.3 kcal/mole which is a much more reasonable reflection of the appreciable resonance stabilization in this compound. Hence this -16.3 kcal/mole becomes the value to use as a ring correction to thiophene derivatives rather than the

previous value of + 1.7 kcal.

Table 2 lists values of ΔH°_{f298} and S°_{298} for key divalent molecules and related radicals containing sulfur. The values of ΔH°_{f} for S, S_2, and SO are derived spectroscopically and are probably reliable to $\pm$ 0.1 kcal. For the radical SH, the value shown of 35 $\pm$ 1 kcal has been adopted. This value derives from a reassessment of the kinetic data on ϕCH_2SH, CH_3SH, and C_2H_5SH (11) and for once is in good agreement with data on electron impact. Of these three kinetic studies the first on ϕCH_2SH is the most reliable, but the extraction of a bond strength requires a scaling of the Arrhenius parameters to a reasonable A-factor of about 10^{15} sec^{-1} and an assignment of the scaled activation energy to the ΔE for the fission reaction. This latter is an important assumption which seems in good agreement with the best current data on radical recombination. It accounts for discrepancies of the order of about 1.5 kcal between the ΔH°_{f} for a number of radicals listed (12) and the values listed in this paper and in Ref. 13. It also accounts for the much larger discrepancies between the ΔH°_{f} for CH_3S and ϕS listed here and those in earlier reviews. The values listed here are from recent studies using VLPP techniques (14) which yield high pressure kinetic parameters in excellent agreement with values of the absolute values of the rate constants from earlier studies (11) which employed the toluene carrier technique. The assignment of the observed, "scaled" activation energy to ΔE_T for the overall fission at reaction temperature, together with a correction of ΔH_T to room temperature ΔH_{298} based on an estimated ΔC_p, lead to a change from earlier values of about 4 kcal. It would be difficult to justify a change in the ΔH°_{f298} for these radicals by more than the indicated uncertainties.

Kende et al (20) have measured the rates of fission of $(CH_3S_2)_2$ in toluene at 65°C using a radical scavenger to follow the first order reaction.

$$(CH_3S_2)_2 \underset{+1}{\overset{1}{\rightleftharpoons}} 2\ CH_3SS\cdot$$

They reported $k_f = 5 \times 10^{17-36.6/\theta} sec^{-1}$ where f is the efficiency with which the radicals are scavenged outside the initial cage and $\theta = 2.303RT(kcal/mole)$. Their A-factor is too large by about 10^2, and since their temperature range was very limited (30°C), the Arrhenius parameters have been scaled to $A = 5 \times 10^{15}$ sec^{-1}

TABLE 2. ΔH°_{f298} AND S°_{298} OF SOME MOLECULES AND RADICALS OF DIVALENT SULFUR*

Reference	Species	ΔH°_{f298} (E strain)†	S°_{298}
(6)	S	66.3	40.1
(6)	S_2	30.7	54.5
(15)	cyclo-S_3	32.5 ± 1 (22.9)	63 ± 1.5
(15)	cyclo-S_4	31 ± 2 (18.4)	72 ± 2
(7,15)	cyclo-S_6	24.5 (5.3)	84.9
(7)	cyclo-S_8	2.45 (-1.1)	103.0
(6)	SH	35± 1	46.7
(7)	H_2S	-4.9	49.2
‡	HS_2	[22.1 ± 1]	[61.4]
(16,7)	H_2S_2	3.8	62.3
‡	HS_3	[25.3 ± 1]	[74.8]
(16)	H_2S_3	7.4	[75.7]
(16)	H_2S_4	10.6	[89.1]
(6)	SO	1.2	53.0
‡	S-OH	[5 ± 4]	[57 ± 1]
‡	$S(OH)_2$	[-67 ± 4]	[70 ± 1]
(6)	SF	3 ± 2	53.8
(6)	SF_2	-71 ± 3	61.6
‡	SCl	[36.5 ± 2]	57.3
(7)	SCl_2	-4.7	67.2
‡	SBr_2	[5 ± 4]	
(6)	FS-SF	-80 ± 10	70.3
(5)	S_2Cl_2	-4.7	76.4
(7)	S_2Br_2 (ℓ)	-3	
	" (g)	[+9]	

(continued)

TABLE 2. (continued)

Reference	Species	ΔH°_{f298} (E strain)†	S° 298
(17)	SN	68 ± 5	53.1
(18)	SC	64.8	50.3
(6)	CS_2	28.0	56.8
(6)	CSO	-33.1	55.3
(19)	CH_2=S	24.3	[56 ± 1]
(14)	CH_3S	34.2 ± 1.5	57.6
(4)	CH_3SH	-5.4	61.0
‡	CH_2=CHSH	[21.0 ± 2]	[67 ± 1]
(4)	CH_3SCH_3	-8.9	68.3
(7)	C_6H_5SH	-11.0	70.8
(14)	C_6H_5S	56.8 ± 1.5	76.5
(4)	C_6H_5SH	26.7	80.5
(7)	cyclo-$\overbrace{CH_2CH_2S}$	19.7 (19.5)	61.0
(4)	$C_6H_5CH_2SH$	22.9	[91.0]
(4)	$(C_6H_5)_2S$	55.3	
‡	$CH_2(SH)_2$	[8 ± 2]	
‡	CH_3S_2	[17.3 ± 1]	
(7)	CH_3SSCH_3	-5.8	80.5
(4)	$C_6H_5SSC_6H_5$	58.4	
‡	CH_3SSS	[20.5 ± 1]	
‡	$CH_3S_4CH_3$	[0.4 ± 1]	
(4)	CH_3COSH	-43 ± 1	74.9

(continued)

TABLE 2. (continued)

Reference	Species	ΔH°_{f298} (E strain)†	$S^{\circ}298$
‡	HCOSH	[-30 ± 1]	
‡	$(CH_3O)_2S$	[-59 ± 5]	
‡	CH_3SCL	[-6.8 ± 1.5]	
‡	CH_3SSCl	[-5.1 ± 1.5]	
‡	C_6H_5SCl	[25.3 ± 1.5]	
‡	$C_6H_5S_2Cl$	[27 ± 1.5]	
(8)	$(NH_2)_2C{=}S$	-6.0	72.4
(7)	$HNC{=}S$	30.0	59.2
(7)	$CH_3NC{=}S$	31.3	69.3
(7)	CH_3SCN	38.3	[69 ± 1]
(4)	$[(C_2H_5)_2NS]_2$	-16.5 ± 1.5	
(4)	$(CNS)_2$	82.3	

* All species are ideal gas, standard states unless otherwise specified. ΔH°_f are in kcal/mole, S° in cal/mole $^{\circ}K$.

† Values in parentheses are ring strain energies.

‡ Values in brackets have been estimated by the author; see text for details.

(comparable to peroxide fissions) and E = 33.6 kcal/mole. This latter value is in excellent agreement with values of 32.8 kcal for the S-S bond in liquid sulfur deduced from measurements of radicals in liquid sulfur (21). It will be assumed that the gas phase value has the same value as has been frequently observed for the fission of nitrites and peroxides. Then using group additivity (13) to deduce a value for ΔH°_{f298} (MeS_4Me) = 0.4 kcal/mole, the value of ΔH°_{f298} ($CH_3SS^{\cdot}$) = 17.3 $\pm$ 1 kcal/mole shown in Table 2 has been deduced. This value together with group additivity yields the value ΔH°_{f298} ($HSS^{\cdot}$) = 22.1 $\pm$ 1 kcal/mole (Table 2) and the values also shown in Table 2 for $HS_3^{\cdot}$ and $CH_3S_3^{\cdot}$.

Similar values have been obtained from the same data by Friswell and Gowenlock (22). Note that a slightly different value has been used for the $\underline{S}$-$(S)_2$ group than that listed in Ref. 13, namely ΔH°_{f298} ($\underline{S}$-S_2) = 3.2 kcal/mole. This is based on the ΔH°_f data for the sulfanes (16,23), which indicate a very consistent value for this group up to H_2S_6. This value for the $\underline{S}$-$(S)_2$ group, together with the observed value for cyclo-S_3 (Table 2), leads to a value of 22.9 kcal for the strain energy in the S_3 ring. This is comparable to values of 17.7 to 21 reported for the various ethylene sulfides (8). This new group value has been used to find strain energies of 5.3 kcal in the c-S_6 ring and -1.1 kcal in the c-S_8 ring.

A very useful guide to thermochemistry comes from consideration of the relative electronegativity of bonds. The SH group and Br atoms are expected to have similar electronegativities and similar radii, and in fact the dipole moments of HBr and H_2S are 0.82 and 0.97 Debye respectively (24), while the H-Br and H-S bond lengths are 1.415 and 1.345 Ang, respectively (25). CH_3Br and CH_3SH have similar dipole moments of 1.81 and 1.52 Debye, respectively (24); the C-S and C-Br bond lengths in these compounds are 1.82 and 1.93 Ang, respectively (25). There are close similarities in the bond dissociation energies in these compounds. A thermochemical datum which also parallels the electronegativities of atoms, X is the difference in the values of ΔH°_f for the compounds HX and CH_3X.

It is observed that when X changes from a very electronegative element to a very electropositive element, the difference ΔH°_f (HX) - ΔH°_f (CH_3X) changes from a negative to a very positive quantity. This type of relation appears to hold true whether or not X is a single atom or part of a more complex group.

A typical range of values for this difference is illustrated by the data in Table 3. Table 3 shows that neighboring groups can exert an important influence on these differences. An excellent example is provided by CH_3 and CF_3. Similarly, while CH_3 for H substitution in HOH makes ΔH°_f more positive by 9.8 kcal, a second CH_3/H substitution increases ΔH°_f by only 4.0 kcal. The same influence of substitution is seen in the nitrogen series and in the sulfur family. This influence of nonbonded, next-nearest neighbors has been rationalized as arising from a change in effective charge on the central atom (26-29), hence its polarity.

As the polarity of the central atom goes from very negative to very positive values, the CH_3/H substitution covers a range of from -10 to +14 kcal/mole. Such a relation permits us to estimate ΔH°_f for compounds with uncertainties of about $\pm$ 2 kcal/mole. Thus we can estimate for the unknown H-NO_2 isomer of nitrous acid (HONO) a ΔH°_f = -6 $\pm$ 2 kcal/mole based on the known ΔH°_f (CH_3NO_2) = -17.9 kcal/mole. This accounts very well for the inability to prepare this isomer, since it is about 12 kcal less stable than HONO for which ΔH°_f = -18.3 kcal/mole and in which the H atom is likely to be quite labile.

Such analogies permit us to estimate ΔH°_f for $CH_2(SH)_2$ from the value of CH_2Br_2 as 6 $\pm$ 2 kcal (Table 2). We shall make frequent use of these relations and for convenience we shall refer to groups that show similar thermochemical behavior as homothermal. The alkyl groups CH_3, ethyl, n-propyl, etcetera form a homothermal family. Estimating from the relations in Table 3, R-SH compounds (where R has about the polarity of carbon compounds) should differ in ΔH°_f from R-Br compounds by 4.0 $\pm$ 0.3 kcal. This is true for R=H, CH_3, and C_2H_5 (Table 3) and appears to be true for R-C_2H_3 for which the ΔH°_f (C_2H_3SH) has been estimated by other methods. It is therefore somewhat surprising that the phenyl compounds ΔH°_f differ only by 1.7 kcal, since vinyl and phenyl have about the same kind of carbon atoms (27). However, the uncertainty in $\Delta H^\circ_f(C_6H_5Br)$ is at lest 2.0 kcal and may be the source of the apparent inconsistency. ΔH°_f (CH_3COBr) is 2.6 $\pm$ 1.5 kcal lower than ΔH°_f (CH_3COSH), which is well within the expectations of our Br/SH substitution rule.

Using the H/CH_3 substitution value observed for HCOOH and CH_3COOH (Table 3), ΔH°_f(HCOSH) = -30 $\pm$ 1 kcal can be deduced and is shown in Table 2.

TABLE 3. EFFECT OF POLARITY AND ELECTRONEGATIVITY ON DIFFERENCES IN HEATS OF FORMATION BETWEEN HYDROGEN (HX) AND METHYL DERIVATIVE (CH_3-X)

X	$\Delta H_f^o(HX)$ *	$\Delta H_f^o(CH_3X)$	$\Delta(\Delta H_f^o)$
F	- 64.8	- 55 ± 2	- 9.8 ± 2
OH	- 57.8	- 48.0	- 9.8
$O(SO_2)CH_3$	-170.5	-164	- 6.5
$O(CO)CH_3$	-103.8	- 98	- 5.8
NH_2	- 11.0	- 5.5	- 5.5
OCH_3	- 48.0	- 44.0	- 4.0
ONO_2	- 32.1	- 28.6	- 3.5
Cl	- 22.0	- 19.6	- 2.4
$NH(CH_3)$	- 5.5	- 4.5	- 1.0
O_2H	- 32.6	- 31.3	- 1.3
$NH(CH_3)$	- 5.5	- 4.5	- 1.0
Br	- 8.7	- 9.5	0.8
SH	- 4.8	- 5.4	0.6
$N(CH_3)_2$	- 4.5	- 5.9	1.4
CH_3	- 17.9	- 20.2	2.3
I	6.3	3.3	3.0
SCH_3	- 5.4	- 8.9	3.5
C_2H_5	- 20.2	- 24.8	4.6
S_2H	3.8	- 1.0[a]	4.8
n-C_3H_7	- 24.8	- 30.2	5.4
C_2H_3	12.5	4.9	7.6
C_6H_5	19.8	12.0	7.8
NO	23.8	16	8
$COCH_3$	- 39.7	- 51.7	12.0
CN	32.3	[19 ± 2]	13 ± 2
COOH	- 90.5	-103.8	13.3
CF_3	-167	-178	11
SiH_3	8	- 4	12
SnH_3	39	[28 ± 3]	11 ± 3

* All values in kcal/mole. Data taken from sources listed in Table 2. Values in brackets are estimated by author.

In the first long row of the periodic table, one of the rather startling early observations on bond dissociation energies (30) was the weakness of the single bonds between the iso-electronic groups NH_2, OH, and F. These are among the weakest single bonds in the periodic table and decrease uniformly in the sequence CH_3-CH_3, (88), NH_2-NH_2, (70), HO-OH, (50), F-F, (38). There is a comparable decrease in bond strengths in the related sequence in the second row SiH_3-SiH_3, PH_2-PH_2, HS-SH, Cl-Cl, but the bonds range from 0 to 20 kcal stronger than their first row group analogues. This tendency has been rationalized on electrostatic grounds as arising from the repulsion of nonbonded lone pairs. In molecular orbital terms the equivalent explanation comes from the increasing destabilization of antibonding electrons. The increased bond strengths in the symmetrical second row compounds is then explained on the basis of a decreased repulsion of the long pair electrons arising from their greater separation in the larger radius, second row elements. This larger radius of the second row elements compared to first row elements should also lead to both weaker sigma and pi bonds when the lone pair effects can be eliminated. As we shall see, the data reflect this but the effects are much smaller than might have been anticipated.

Table 4 lists the few compounds containing S atoms double bonded to some other atom or group. The S bond dissociation energies in these compounds are compared with those of their oxygen analogues. Notice that the S-S bond in S_2 is some 17 kcal weaker than the O-O bond in O_2. As expected from considerations of both electronegativity difference and lone pair repulsion, the bond dissociation energy in SO is greater than in either homonuclear molecule.

Even larger differences exist in the CH_2O and CH_2S pair, where there is no lone pair repulsion and in the CO, CS pairs which are really better described as triple bonded compounds.

A measure of the relative abilities of S and O atoms to donate electrons and act as Lewis bases is seen on comparing the C-O bond strengths in CH_2O with CO_2. The 45 kcal apparent greater bond strength in the former compound can be associated with the extra pi bond formation in CO. The greater C-O bond strength in SCO compared to OCO is then a reflection of the weaker base properties of S in C=S. The same behavior is seen in the sulfur analogues. The

TABLE 4. A COMPARISON OF DOUBLE BOND STRENGTHS IN SOME DIVALENT SULFUR COMPOUNDS WITH OXYGEN ANALOGUES

Sulfur Compound	- S Bond Dissociation Energy	Oxygen Analogue	- O Bond Dissociation Energy
S_2	102.5	O_2	119.2
SO	124.7	OS	124.7
SC=S	103.4	SC = O	157.5
CH_2=S	129 ± 5	CH_2 = O	172 ± 3
OC=S	73.3	OC = O	127.2
C=S	173	C = O	257
CH_3NC=S	71		

CH_2=S is stronger than the SC=S bond, while the OC=S bond is one of the weakest S bonds observed.

In the sequence CO_2, COS, CS_2, there is a constant 61 kcal change in ΔH°_f on replacing O by S. This difference is maintained in the related pair of very polar compounds $CO(NH_2)_2$ and $CS(NH_2)_2$ for which data exist in aqueous solutions (7), which suggests that it should be the same in the paired compounds CH_3NCO/CH_3NCS and HNCO/HNCS. On this basis ΔH°_{f298} [HNCO(9)] = -30 kcal is assigned. This would make it about 6 ± 2 kcal/mole more stable than the isomeric HOCN (7).

Table 5 lists some S-H bond dissociation energies derived from the data on ΔH°_f shown in Table 2 and the known ΔH°_f of H and other free radicals (Ref. 13). A number of features are noteworthy. In the saturated mono sulfur compounds RS-H, the S-H bond is 92 kcal, independent of the nature of R. In the oxygen homologues a similar behavior is seen except in the case of HOH where the O-H bond has a value of 119 kcal in contrast to ROH compounds where it is 104 kcal. This is a reflection of the polarity effects already discussed in connection with Table 3.

Phenyl exerts a bond-weakening effect on adjacent S-X bonds analogous to its effect on CH_2 and O, reflecting a delocalization of the ring electrons and charge donation to the radical center. The effect in $\phi S^{\cdot}$ measured against saturated $RS^{\cdot}$ radicals is seen to be 10 kcal, significantly lower than the 13.5 kcal

TABLE 5. SOME S-H BOND DISSOCIATION ENERGIES FOR DIVALENT SULFUR

RS-H	Bond Dissociation Energy	RS-H	Bond Dissociation Energy
$^{\cdot}S$-H	83.6 ± 1	HS_2-H	70 ± 1.5
HS-H	92.0 ± 1	alkyl S_2-H	70 ± 1.5
CH_3S-H	92 ± 1.5	HS_3-H	70 ± 1.5
C_2H_5S-H	92 ± 2	HS_{3+n}-H	70 ± 1.5
alkyl S-H	92 ± 2	alkyl S_{3+n}-H	70 ± 1.5
C_6H_5S-H	82 ± 1.5		
$^{\cdot}S_2$-H	60.5 ± 1.5		

observed in CH_2 and the 17 kcal found in O (31). As will be seen, this is a relection of the weaker pi bond between C and S.

Sulfur also exerts a bond-weakening influence on adjacent bonds; the S-H bond in H_2S_{n+1} is some 22 kcal weaker than the other S-H bonds. This difference can be identified with the partial double or pi bond formed in the radical $R\text{-}\overset{\frown}{S}\text{=}S^{\cdot}$ and reflects the Lewis base character of divalent sulfur. It can be compared with the similar behavior of O atoms in H_2O_2 where the effect relative to ROH is about 14 kcal (30).

The behavior of the S-H bond strengths is also paralleled by the S-C bonds listed in Table 6. Saturated groups R attached to S have little or no influence on the adjacent RS-CXYZ bond for a given X, Y, and Z. Unsaturated groups R or groups with lone pairs or conjugated pi electrons exert a bond-weakening effect comparable to their effect on S-H bonds. Of particular interest for the symmetrical

compounds X_2S is the observation that the first bond dissociation energy is about 8.5-11.0 kcal stronger than the second. This is opposite in behavior to the oxygen analogues R_2O where the second bond in RO· is about 8 kcal stronger than the first bond. This inverse behavior can again be seen as arising from polarity effects on the ΔH°_f of the two sets of compounds R_2O and R_2S. We note from Table 3 that the substitution of CH_3 for H in H_2O and CH_3OH increases ΔH°_f while the opposite is the case for CH_3/H substitution in H_2S.

Adjacent sulfur atoms again have a bond-weakening effect on S-C bonds. From Table 6 we see the bond lowering is 20 kcal compared to 22 kcal for the S-H bonds. In principle these two numbers should be the same, and within the experimental uncertainty they can be represented by their average of 21 $\pm$ 1 kcal. This is a measure of the relative self-consistency of the ΔH°_f data for both the molecule and radical species involved and the application of group additivity. A similar consistency is found on comparing the S-Cl bond strengths in MeS-Cl and MeS_2-Cl (Table 7). The heats of formation of these mixed compounds have been estimated by methods of bond additivity from ΔH°_f for SCl_2 and S_2Cl_2. The differences in these two bond strengths is estimated at 19 $\pm$ 3 kcal, in good agreements with the 21 $\pm$ 1 kcal difference calculated for the S-H and S-C series. However, a comparison of the similar S-S bonds in H_2S_2 and H_2S_3 (Table 7) reveals a difference of only 16 $\pm$ 2.5 kcal with a similar value for the HS_2-S_2H/HS_2-SH difference. These are real discrepancies, which reflect the fact that H_2S does not follow the bond additivity rules followed by other sulfanes but is instead more stable by almost 6 kcal.

Sulfur-sulfur bonds follow the same general trends noted for the S-H and S-C bonds. They are, however, significantly stronger in the alkyl disulfides than in the hydrogen disulfanes (Table 7). This effect disappears after R_2S_4 and thus is strictly a neighboring S-S effect.

Very few other S bond strengths are known, Table 7 listing the ones that have been measured. A number of S-Cl bonds have been estimated by additivity methods plus the observation that the first R-S bond dissociation energies exceed the second in the R_2S_2 compounds by about 9.5 $\pm$ 1 kcal.

This last observation, which appears to hold for R = H, alkyl, aryl, SH, SCH_3, and Cl, indicates the strength of the pi bond in S_2 and related compounds.

TABLE 6. SOME S-C BOND DISSOCIATION ENERGIES FOR DIVALENT SULFUR

RS-C	Bond Dissociation Energy	RS-C	Bond Dissociation Energy
$^{\cdot}S\text{-}CH_3$	66 ± 1.5	$CH_3S\text{-}CH_3$	77 ± 1.5
$^{\cdot}S\text{-}C_2H_5$	63 ± 2	alkyl S-CH_3	77 ± 1.5
$^{\cdot}$S-alkyl	63 ± 2	$C_6H_5S\text{-}CH_3$	67.4 ± 1.5
$^{\cdot}S\text{-}C_6H_5$	88.5 ± 1.5	$CH_3S\text{-}C_2H_5$	74 ± 1.5
		n-alkyl S-C_2H_5	74 ± 2
$HS\text{-}CH_3$	75 ± 1.5		
$HS\text{-}C_2H_5$	72 ± 1.5	n-alkyl S-iPr	73.5 ± 1.5
HS-iPr	72 ± 1.5	n-alkyl S-tBu	71 ± 1.5
HS-tBU	69 ± 1.5	$CH_3S\text{-}C_6H_5$	89.2 ± 2
$HS\text{-}C_2H_3$	83 ± 3	$CH_3S\text{-}CN$	97 ± 1.5
$HS\text{-}C_6H_5$	86.5 ± 2		
HS-(CO)H	74 ± 2	$HS_2\text{-}CH_3$	57 ± 1.5
$HS\text{-}COCH_3$	73 ± 2	alkyl $S_2\text{-}CH_3$	57 ± 1.5
$^{\cdot}S_2\text{-}CH_3$	47.5 ± 1.5	alkyl $S_2\text{-}C_2H_5$	54 ± 1.5
$^{\cdot}S_2\text{-}C_2H_5$	44.5 ± 1.5	alkyl $S_2\text{-}C_6H_5$	69.5 ± 1.5
$^{\cdot}S_2\text{-}C_6H_5$	60 ± 2	$CH_3S\text{-}CN$	97

The difference between the first and second bond dissociation energies in symmetrically substituted alkanes RCH_2CH_2R can be equated to the pi bond energy formed in the C_2H_4 product (30). It has been shown to be a transferable quantity independent of the groups R (32). In the case of unsymmetrical olefins or heteronuclear olefins such as $CH_2{=}O$ or $HN{=}O$ or $CH_2{=}NH$, the bond strengths in the two possible radicals, for example $CH_3O^{\cdot}$ and $\dot{C}H_2OH$ must be known. For

TABLE 7. SOME S-S AND OTHER BOND DISSOCIATION ENERGIES FOR DIVALENT SULFUR

RS-SR'	Bond Dissociation Energy	RS-X	Bond Dissociation Energy
HS-SH	66 ± 2	$^{\cdot}S$-F	82 ± 3
CH_3S-SCH_3	74 ± 2	FS-F	92 ± 3
alkyl S-S alkyl	74 ± 2	CH_3S-Cl	[70 ± 3]
		CH_3S_2-Cl	[51 ± 2.5]
HS_2-SH	50 ± 2	ClS_2-Cl	[51 ± 2]
HS_2-SCH_3	54 ± 2	$^{\cdot}S_2$-Cl	[42 ± 2]
HS_2-S alkyl	54 ± 2	C_6H_5S-Cl	[31 ± 2.5]
HS_2-SC_6H_5	44 ± 2	ClS-Cl	[70 ± 3]
		$^{\cdot}S$-Cl	[60 ± 2]
HS_2-S_2H	33.6 ± 2	$^{\cdot}S$-Br	[52 ± 4]
alkyl S_2-S_2 alkyl	33.6 ± 2	BrS_2-Br	[42 ± 4]
RS_{2+n}-$S_{2+m}R$	33.6 ± 2	$^{\cdot}S$-OH	[70 ± 4]
		HOS-OH	[81 ± 4]
HS-$S^{\cdot}$	79 ± 1	$\phi N{=}N$-$S\phi$	[29 ± 1][66]
CH_3S-$S^{\cdot}$	83 ± 1	$(Aryl)_3CS$-NO	[25 ± 1][67]
C_6H_5S-$S^{\cdot}$	74 ± 1.5	CH_3S-NO	[25 ± 1]
FS-SF	61 ± 4		
C_6H_5S-SH	61 ± 1.5		
C_6H_5S-SCH_3	65 ± 1.5		
C_6H_5S-SC_6H_5	55 ± 1.5		
RS_2-$S^{\cdot}$	63 ± 1		

symmetrical pi bonds there may be significant stabilization in the intermediate radical as in the radicals $RS_2^{\cdot}$. This leads to weakening of the first bond in RS_2-R and strengthening in the second bond in R-$S_2^{\cdot}$, hence a smaller difference DH°_1-DH°_2 by double the amount of stabilization in the radical.

If the stabilization energy in $RS_2^{\bullet}$ is assumed to be 21 $\pm$ 1 kcal the pi bond strength in S_2 can be estimated as the nearly universal DH°_1 -DH°_2 = 9.5 kcal + 2 X 21 = 51.5 $\pm$ 2 kcal. A similar calculation for perioxides yields a value of 71 $\pm$ 1.5 kcal for the pi bond strength in O_2. This latter is very reasonable compared to pi bond strengths observed in olefins (~60 kcal), acetylenes (~72 kcal), and aldehydes (~76 kcal).

The same reasoning can be applied to the relation between CH_3SH and CH_2=S. From Table 2 the sum of the C-H and S-H bonds that are broken in the process can be estimated to be 133.5 $\pm$ 3 kcal. The S-H bond is known to be 92 kcal (Table 5), while the C-H bond is not known. In fact, it can be anticipated that the C-H bond will be weakened by the adjacent S atom relative to the C-H bond in ethane. If a value of 98 kcal for a hypothetically unperturbed C-H bond strength in CH_3X is adopted, then 190 kcal can be estimated to be the sum of the C-H + S-H bonds in CH_3SH in the absence of interactions. The difference between this value and the experimental 133.5 $\pm$ 3 can then be taken at the pi bond strength in CH_2S, namely, 56.5 $\pm$ 3 kcal. This is very close to the value of the pi bond strength in olefins and is consistent with the observation that $\Delta H^{\circ}_f(CH_2 = S)$ is very closs to the average of ΔH°_f for S_2 and C_2H_4. The average is 21.6 kcal/mole compared to the 24 $\pm$ 3 reported (Table 2).

The above value of the C=S pi bond strength is only 3 $\pm$ 3 kcal lower than the values observed in olefins and can be used to rationalize the fact noted earlier that $C_6H_5S^{\cdot}$ has a stabilization energy about 3.5 kcal lower than found in $C_6C_5\dot{C}H_2$, which is in turn about 3.5 kcal weaker than the value found in $\phi O^{\cdot}$. On this basis it can be predicted that the S-H bond strength in CH_2=CHSH will be about 84 kcal reflecting an estimated 8 kcal "allylic" stabilization energy in the CH_2=$CHS^{\cdot}$ radical.

The pyrolysis of divalent sulfur compounds has proven fairly difficult to interpret. Part of this difficulty has come from the occurrence of parallel radical and molecular path (11) as well as appreciable sensitivity to vessel wall condition and traces of oxygen. Compounds containing pi bonds to sulfur

are extremely susceptible to polymerization (19,33), and this is generally a heterogeneous process, probably acid and/or base catalyzed. One known but unappreciated difficulty arises from reactions producing elementary sulfur as a product (34), such as in the pyrolysis of episulfides which produce olefins plus sulfur.

The stable form of sulfur in the gas phase is S_8 if it is below its vapor pressure. But the equilibrium

$$c\text{-}S_8 \overset{a}{\rightleftharpoons} 4S_2$$

is readily attained and leads to a small but significant and almost constant concentration of the very reactive S_2 species:

$$(S_2) = K_{eqa}{}^{1/4}(S_8)^{1/4}$$

Since (S_2) is proportional to $(S_8)^{1/4}$, a fourfold change in (S_8) gives only a 40% change in (S_2). ΔH_a = 24.7 kcal calculations from the data in Table 2 , show that at 500°K, 1 torr of S_8 will be in equilibrium with 2.5 millitorr of S_2. It is very likely that the apparent first order thermal decomposition of episulfides proceeds by a complex chain reaction in which the rate determining step is bimolecular:

$$\overbrace{RCH\text{-}CH_2S} \overset{i}{\rightleftharpoons} RCH = CH_2 + S$$

$$S + \overbrace{RCH\text{-}CH_2S} \overset{1}{\rightarrow} \dot{R}CH\text{-}CH_2S_2\cdot \overset{2}{\rightarrow} RCH = CH_2 + S_2$$

$$S_2 + \overbrace{RCH\text{-}CH_2S} \overset{3}{\underset{(slow)}{\rightarrow}} S_3\cdot + RCH = CH_2$$

$$S_3\cdot \overset{\text{fast}}{\rightsquigarrow} 3/8\ S_8$$

$$1/4\ S_8 \overset{\text{fast}}{\rightleftharpoons} S_2$$

The rate constant for sulfide disappearance is then:

$$\frac{-d(RC_2H_3S)}{dt} = k_i\,(RC_2H_3S) + k_3k_a{}^{1/4}(S_8)^{1/4}(RC_2H_3S)$$

where after a very brief induction period during which S_2 and S_8 build up, the first term becomes negligible and $(S_8)^{1/4}$ varies only slightly. A value of E_3 in the range 11-14 kcal would then account quite well for the observed apparent first order rate constants. Reaction 3 is close to being thermoneutral for most R and presumably goes through a biradical $R\text{-}\dot{C}H\text{-}CH_2S_3^{\bullet}$ intermediate. It is also therefore reversible and might show a resultant inhibiting effect on the overall reaction as product olefin is produced, which might then obscure the small auto-catalytic effect due to increasing S_8.

A final observation is in order regarding the strain energies in small ring compounds containing sulfur. Compared to first row ring compounds containing C, O, N where strains seem to be dependent only on ring size, rings with a single S atom have about 8 kcal less strain than the carbon analogue. What is surprising then is that this seems to hold true for rings with 3 or 4 sulfur atoms as well.

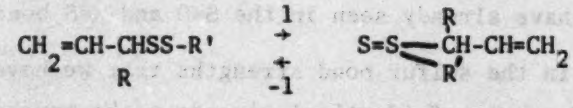
SECTION 3

THERMOCHEMISTRY OF TETRAVALENT SULFUR COMPOUNDS

The higher valence states of sulfur are conspicuous by the fact that they are known only in the form of oxygen or fluorine derivatives. These can be classified as derivatives of >SO or $>SF_2$ in the tetravalent states or $>SO_2$, $>SOF_2$, and $>SF_4$ derivatives in the hexavalent states. As such they are strongly reminiscent of the noble gas compounds and the higher valence states of the halogens. Relatively little is known about the thermochemistry of the tetravalent sulfur compounds, and most of this is of lower quality than that for divalent suflur. Most of the data available is shown in Table 8. One of the important compounds in this table is sulfurous acid for which ΔH°_f (aq.) is well known, although some uncertainty still exists as to how much H_2SO_3 in aqueous solution is better considered the isomer $H_2O \cdot SO_2$. Based on data for differences in ΔH°_f between gas phase and aqueous solutions for comparable species, a difference of 18.5 $\pm$ 3 kcal for the two phases has been estimated. This gives a value for the gas phase species that appears to be consistent with other related values.

An interesting example of the effect of electronegative species on the relative stability of the two and four valence states of sulfur is seen in the isomeric compounds FSSF and SSF_2. Both of these compounds can be prepared, presumably pure (35). However, if the liquid FSSF is allowed to warm up above 0°C, it spontaneously changes over to the more stable SSF_2. In contrast dialkyl disulfides RSSR' appear to be stable and known only in the indicated bonding state. However, substantial evidence indicates that the thiosulfoxide form SS(R)R' is probably not more than 10 kcal less stable.

Hoffle and Baldwin (36) have convincingly demonstrated that allyl disulfides can undergo a Cope-type rearrangement with a thiosulfoxide intermediate



This intermediate can be trapped by $P\phi_3$ to give $SP\phi_3$ and $R'SCHRCH{=}CH_2$. At high enough concentrations of the trapping agent $P\phi_3$, the reaction is observed to be first order with $\Delta H^{\ddagger} = 20 \pm 1$ kcal and $\Delta S^{\ddagger} = -9 \pm 1$ eu. If the $P\phi_3$ reaction is assumed to have an activation energy of about 3 to 4 kcal, then the thiosulfoxide must lie not more than 10 kcal in heat of formation above the disulfide. This then leads to the estimates for ΔH°_f [S=S(ME)$_2$] and $\Delta H^{\circ}_f(S{=}SH_2)$ shown in Table 8. It is interesting to speculate that, since the relative stability of thiosulfoxides seems to shift with the electronegativity of the groups attached to S, compounds like $(RO)_2S{=}S$ might be stable relative to their disulfide isomers, while somewhere in the sequence Br_2S_2, Cl_2S_2, one might find the two isomeric forms close together in ΔH°_f and hence coexisting.

The only bonds for which dissociation energies are known with any certainty are some of the S=O double bonds; these are tabulated in Table 9. Along with them are listed the less certain S=S bonds in thiosulfoxides. It can be seen that as the electronegativity of the groups attached to the tetravalent sulfur decreases, the S=O bond strength decreases along with it. The same behavior, although with much less certainty, is displayed by the S=S bonds in thiosulfoxides. A possible exception to this is the observation by Mislow and Miller (38) that optically active aryl-SO-CH_2 aryl will racemize with a rate constant much larger than for nonbenzylic type substituents. From the observed A-factor and observation of radical recombination products, they deduce in fact that the racemization is proceeding via a bond fission. Using their rate constant and an assigned A-factor of $10^{15.5}$ sec^{-1}, an estimate of the activation energy of 36 kcal can be made. Assuming the same value in the gas phase and neglecting substituent effects in the aryl groups, an estimate of $\Delta H^{\circ}_f(\phi SO_2)$ as shown in Table 8 can be made. The bond strengths deduced in this fashion are reasonably consistent with those deduced by other methods as will be seen in the following.

The best solution under these conditions is to list the sum of the two bonds dissociation energies and perhaps speculate on how they may differ. This is shown in Table 10. They show the same decrease in binding energy with electronegativity that we have already seen in the S=O and S=S bond strengths.

The general tendency in the sulfur bond strengths that we have considered so far is for the first of a pair of identical ligands to be more strongly bound than the second. The one set of data that exists in the tetravalent

TABLE 8. HEATS OF FORMATION AND ENTROPIES OF SOME MOLECULES AND RADICALS OF TETRAVALENT SULFUR

(Reference)	Species	ΔH^{o}_{f298}	S^{o}_{298}
(6)	SO_2	-70.9	59.3
(7)	SO_2(aq)	-77.2	38.7
(2,6)	S_2O	-10	63.8
(6)	SOF_2	-130 ± 5	66.7
(7)	$SOCl_2$	-51	74.0
(7)	$SOBr_2$	-21.8	
(6)	SF_4	-183 ± 5	71.6
(7)	$SO(HO)_2$(aq)	-145.5	55.5
	$SO(HO)_2$	[-127 ± 3]	[69]
(4)	$SO(OMe)_2$	-115.5	
(4)	$SO(OEt)_2$	-131.9	
37	$\phi S(SO)\phi$	[34 ± 2]	
37, 38	C_6H_5SO	[13 ± 2]	
	$(\phi SO)_2$	[11 ± 4]	
(4)	$\phi CH_2SO\phi$	20.6	
	$SO\ H_2$	[-16 ± 4]	
(4)	$SO(Me)_2$	-36.0	73.2
	SSF_2	[<-60 ± 6]	
(6)		-96 ± 10	70.0
(6)	SF_3	-119 ± 4	66 ± 1.5
(4)	$SO(Et)_2$	-49.1	
(4)	$SO(C_6H_5)_2$	25.6	
(4)	$SO(NEt_2)_2$	-66.3	
	$S{=}S(Me)_2$	[4 ± 3]	
	$S{=}SH_2$	[10 ± 7]	
	CH_2SO	[-12 ± 5]	

TABLE 9. S=S AND S=O BOND DISSOCIATION ENERGIES IN SULFOXIDE DERIVATIVES

Species	Bond Dissociation Energy	Species	Bond Dissociation Energy
S=O	124.7	H_2S=O	[71 ± 4]
OS=O	132	ME_2S=O	86.6
SS=O	100	Et_2S=O	88.7
F_2S=O	118 ± 6	$(C_6H_5)_2$ S=O	89.3
$(HO)_2S$=O	[118 ± 6]	OS=S	77
$(MeO)_2S$=O	[116 ± 6]	F_2S=S	[>57 ± 8]
Cl_2S=O	105	Me_2S=S	[53 ± 4]
Br_2S=O	[86 ± 4]	H_2S=S	[51 ± 7]
$C_6H_5\dot{S}$=O	[103 ± 2]		
ϕSSOϕ	[83 ± 4]		
ϕSOSOϕ	[83 ± 4]		

TABLE 10. SUM OF SINGLE BOND DISSOCIATION ENERGIES R-S + R'-S IN SULFOXIDES RR'S = O AND THIOSULFOXIDES AND ESTIMATES OF D_1

Species	$D_1 + D_2$	Estimated D_1*	Species	Sum of Bond Dissociation Energies	Estimated D_1*
F_2SO	169	(87)	H_2SO	121 ± 4	(63)
Cl_2SO	110	(58)	Me_2SO	105	(55 ± 2)
Br_2SO	75	(40)	Et_2SO	102	(54)
$[F_2SF_2]$	105 ± 6]	(83 ± 5)	ϕ_2SO	133	66 ± 2
$(HO)_2SO$	146 ± 6	(76)			
$(MeO)_2SO$	125	(65)	F_2SS	[>129 ± 6]	
$(EtO)_2SO$	125	(65)	Me_2SS	95 ± 3	(47 ± 3)
$(Et_2N)_2SO$	122	(63)	H_2SS	125 ± 7	(64 ± 7)
ϕS-SOϕ	-	36	ϕSO	-	67 ± 2

*Values in parentheses indicate estimated value of D_1 based on D_1-D_2 = 5 ± 2. See text.

sulfur group is for successive S-F bonds in SF_4. The data in Table 8 can be used to estimate the first bond dissociation energy as 83 ± 5 while the second becomes 67 ± 5, the difference being 16 kcal in favor of the first. On the other hand, for the thiosulfoxides of CH_3 and H, the first bond dissociation energies can be estimated from the data in Table 10; they suggest within the large uncertainties shown that $D_1 \approx D_2$, although a difference $D_1 - D_2 \sim 8 \pm 3$ would also be compatible with the data.

Data on the pyrolysis of Me_2SO, which is a radical chain process (39), can be employed to yield a value of $DH^\circ(CH_3\text{-}SO(CH_3)) \geq 53$ kcal but ≤ 56 kcal. If we take the mean as 55 ± 2 kcal, then $DH_2^\circ(Me\text{-}SO) = 50 \pm 2$ kcal, which is in reasonable accord with the preceding observations on Me_2SS and SF_4. It would suggest $D_1 - D_2 \sim 5 \pm 1$ kcal in Me_2SO, which in turn suggests that this might be applicable to the other sulfoxides as well.

Additional information comes from the pyrolysis of ethylene sulfoxide (40), which decomposes to ethylene + SO_2 + S in chlorobenzene solution at 100°C. The activation energy was estimated at 36 kcal/mole. However, the overall reaction to eliminate SO is only endothermic by about 25 kcal,

$$\overbrace{CH_2\text{-}CH_2\text{-}SO} \rightarrow C_2H_4 + SO$$

if the strain energy is assumed to be like that in the episulfide, namely 18 kcal/mole. If it is assumed that in R_2SO, $D_1 - D_2 = 5 \pm 1$, then in Et_2SO the C-S bond strength is 53 kcal. Thus the activation energy for ring opening to the biradical is only 34 kcal/mole

$$\overbrace{CH_2\text{-}CH_2\text{-}SO} \overset{1}{\rightleftarrows} \dot{C}H_2\text{-}CH_2\text{-}S\dot{O} \overset{2}{\rightarrow} C_2H_4 + SO$$

The second step in this process is exothermic by 11 kcal and probably has very little activation energy, thus making step 1 rate determining. If ring closing has only a few kcal of activation energy, the data would be compatible with the observations. A concerted process cannot be ruled out. It would be spin forbidden and would involve a crossing of the singlet-triplet surface at an appreciably higher activation energy than the overall endothermicity.

Qualitative rate data on the pyrolysis of trimethylene sulfoxide (41) to give $CH_2 = SO + C_2H_4$ is also in agreement with the biradical mechanism, reaction starting with C-S bond fission to give the unstable $\cdot(CH_2)_3SO$ biradical.

From these estimates of R-SOR' bond strengths, an estimate can be obtained of the pi bond strength in CH_2SO. Starting with CH_3SOCH_3, the sum of the CH_3-$SOCH_3$ (55 $\pm$ 2) and the C-H in the "unperturbed" methyl (98 kcal) as 153 $\pm$ 2 kcal can be estimated. But the overall reaction

$$CH_3SOCH_3 \rightarrow CH_2{=}SO + H + CH_3$$

is endothermic by 110 $\pm$ 5 kcal. Hence the C-S pi bond strength in $CH_2{=}SO$ is 43 $\pm$ 5 kcal, appreciably less than the pi bond strength of 56.5 we have calculated for $CH_2{=}S$.

It is interesting to note that the ϕSO radical has an estimated stabilization energy of only 3 kcal, considerably less than the 9.6 kcal observed in ϕS and also less than the 13 found in ϕSO_2. This would be in accord with the weak pi bond formation in $CH_2{=}SO$ just commented on.

SECTION 4

THERMOCHEMISTRY OF HEXAVALENT SULFUR COMPOUNDS

Hexavalent sulfur compounds can all be represented as derivatives of the $>SF_4$ or $>SO_2$ groups, and they are presented in this fashion in Table 11. The data are again very meager compared to that for divalent sulfur compounds, and their accuracy, with few exceptions, is not better than $\pm$ 2 kcal (8). To interpret oxidation kinetics, thermochemical data for the oxy and peroxy molecules and radicals in this series should be known, but the data are particularly sparse. However, a number of empirical rules will be of assistance. The first is that F and OH turn out to be a homothermal pair. The replacement of OH by F in compounds where the attachment is to an electronegative element X (RXOH→ RXF) results in an increase in ΔH°_f of about 7 kcal. For X=H or CH_3 this reverses to -7 kcal. When X is more positive as in vinyl, phenyl, or carboxyl compounds, substitution of F for OH makes ΔH°_f more negative by about -2 kcal. SO_2 can be fitted into this sequence by observing that $SO_2(OH)_2$ is 4 kcal less stable than SO_2F_2, while $FSO_2(OH)$ is almost precisely the arithmetic mean.

Thus the SO_2 group seems to follow bond additivity rules to about $\pm$ 1 kcal with respect to elements of similar electronegativities such as Cl, F, and OH. On this basis we have estimated ΔH°_f for $Cl(SO_2)OH(g)$ as -133 $\pm$ 1 kcal (Table 11). This appears to be compatible with the known ΔH°_f for the liquid and ΔH°_{vap} extrapolated from $F(SO_2)OH$ (Table 11).

Data on the peroxy sulfuric acids exist only in aqueous solution. If the 40 kcal difference betweenn ΔH°_f(aq.) and ΔH°_f(g) for H_2SO_4 is used as a starting point for extrapolation and consider that $H_2S_2O_8$ is a very strong acid like H_2SO_4, then a difference of 47 $\pm$ 3 kcal for $H_2S_2O_8$ can be estimated, then a value of ΔH°_f (gas) = 273 $\pm$ 3 kcal can be assigned to $H_2S_2O_8$ as shown in Table 11. This value together with group additivity gives a value of -153 $\pm$ 2 kcal for ΔH°_f $(HO(SO_2)OOH)_{gas}$. Further assuming that H_2SO_5 has a difference in ΔH°_f between gas and aqueous states similar to H_2SO_4 leads to $\Delta H^\circ_f(H_2SO_5)_{aq}$ = -193 $\pm$ 3 kcal.

TABLE 11. HEAT OF FORMATION AND ENTROPIES OF SOME MOLECULES AND RADICALS OF HEXAVALENT SULFUR

(Reference)	Species	ΔH°_{f298}	S°_{298}
(6)	SO_3	-94.6	61.3
(6)	SO_2F_2	-181 ± 2	67.8
(6)	SO_2Cl_2	-84.8 ± 0.5	74.3
(6)	SO_2ClF	[-133 ± 5]	72.3
(6)	SF_6	-291.7	69.7
	SF_4Cl	[-177]	
(6)	SF_5	[-218 ± 3]	77 ± 2
(6)		-233 ± 5	
(7)	SF_5Cl	-250.5	76.3
(4)	SO_2H_2	[-64 ± 4]	
(7,6)	$SO_2(OH)_2$		
	(ℓ)	-194.5	37.5
	(aq)	-217.3	4.8
	(g)	-177.0 ± 2	69.1
	SF_5OH	[-290 ± 2]	
(6)	$FSO_2(OH)$		
	(ℓ)	-190.5	
	(g)	-180	71.0
(7)	$ClSO_2(OH)$		
	(ℓ)	-143.7	
	(g)	[-133 ± 1]	
	$F(SO_2)O^{\cdot}$	[127 ± 1.5]	[68.5 ± 1]
	$HO(SO_2)O^{\cdot}$	[-125 ± 2.0]	[72 ± 1]
	SF_4Cl_2	[-205 ± 3]	[78 ± 1.5]
	$^{\cdot}SO_3H$	[-98 ± 3]	[67 ± 1]
(4)	$SO_2(Me)_2$	-88.7	74.2
(4)	$SO_2(OMe)_2$	-164	
(4)	$SO_2\phi_2$	-28.3	
(4)	$SO_2(OEt)_2$	-180.7	
(4)	$SO_2(Et)_2$	-102.5	

(continued)

TABLE 11. (continued)

(Reference)	Species	ΔH°_{f298}	S°_{298}
(4)	$\phi SO_2\text{-}SO_2\phi$	-115	
	cyclo(SO_2-O)	-314	
	$HO(SO_2)O_2H$		
	(aq)	[-192 ± 2]	
	(g)	[-152 ± 2]	[81.5 ± 1]
(7)	$[HO(SO_2)O]_2$		
	(aq)	-320	59.3
	(g)	[-272 ± 2]	[104 ± 2]
(7)	$HO(SO_2)_2OH$		
	(aq)	-286.4	
	(g)	[-246 ± 5]	
	$[F(SO_2)O]_2$		
	(g)	[-276 ± 3]	[101 ± 2]
	$[HO(SO_2)]_2O$	[-282 ± 3]	
	$HO(SO)O_2H$	[-105 ± 5]	
	cyclo $O_2\overline{S\text{-}O\text{-}O}$	[-76 ± 3]	
	biradical SO_4	[-73 ± 5]	
	$HOSO_2O_2^{\cdot}$	[-114 ± 4]	
	$SO_2(O_2H)_2$	[-127 ± 3]	
(37,42)	$C_6H_5SO_2$	[-37 ± 1]	
(37)	$C_6H_5(SO_2)SOC_6H_5$	[-52 ± 2]	
	$C_6H_5(SO_2)SC_6H_5$	[-22 ± 4]	
	$SF_5O^{\cdot}$	[-236 ± 4]	
(43)	SF_4O	[-226 ± 4]	
	$(SF_5O)_2$	-509 ± 5	

Values in brackets have been estimated by the author.

Monger and Redlich have measured the equilibria in aqueous solution (44):

$$H_2SO_4 + HO_2H \rightleftharpoons H_2SO_5 + H_2O$$

and found an apparent equilibrium constant of about 0.1 at 25°C which increased to about 0.2 at 75°C. This latter would suggest $\Delta H \approx +2.8$ kcal and require $\Delta S \approx 5$ e.u. to account for $\Delta G \approx 1.4$ kcal. This would lead to $\Delta H^\circ_f (H_2SO_5)_{aq} = 188$ kcal, in only fair agreement with our previous estimate. However, the best a priori estimates of ΔS° for this equilibrium yield a value of $\approx +13$ e.u. and hence a $\Delta H \approx -2.8$ e.u. The increase in Keq with T would then have to be ascribed to an anomalously high value for ΔC°_p. This latter choice would give $\Delta H^\circ_f (H_2SO_5^\cdot)aq = -193$ kcal, in excellent agreement with an earlier estimate. A resonable reconciliation would be to use -191 ± 2 kcal which leads then to $\Delta H^\circ_{f298}(H_2SO_5)_{(gas)} = -151 \pm 3$ kcal, thence via group additivity to $\Delta H^\circ_{f298}(H_2S_2O_8)_{(gas)} = -270 \pm 6$ kcal. As a reasonable compromise among these values, $\Delta H^\circ_{f298}(H_2S_2O_8)_{(gas)} = -272 \pm 2$ kcal will be used. This then leads to $\Delta H^\circ_{f298}(H_2SO_5)_{(gas)} = -152 \pm 2$ and the other related values shown in Table 11.

Let us note in passing that a similar equilibrium study of formic acid (44)

$$H_2O_2 + HCOOH \rightleftharpoons H_2O + HCO_3H$$

leads to a value for $\Delta H^\circ_f(HCO_3H)$ gas in excellent agreement ($\pm$ 1 kcal) with independent estimates from group additivity and kinetic data on diacyl peroxides (45).

Now making use of the observation that F and OH form a homothermal pair relative to SO_2 with a $\Delta(\Delta H^\circ_f)$ of 2 kcal, $\Delta H^\circ_f[F(SO_2)OO(SO_2)F]_{gas} = -276 \pm 3$ kcal can be estimated.

A number of studies have been made of the reversible dissociation of $F_2S_2O_6 \rightleftharpoons 2FSO_3$ (46), ΔH and ΔS are known with reasonable accuracy. From these measurements and the data already discussed, estimates of $\Delta H^\circ_f(FSO_3^\cdot)_{gas}$ and $S^\circ(FSO_3^\cdot)$ shown in Table 11 can be made as well as the other entropies shown. Finally, the F/OH rule is used to estimate $\Delta H^\circ_f(HOSO_3^\cdot)_{gas} = -125 \pm 2.0$ kcal. Note that this yields a value for the O-H bond dissociation energy in H_2SO_4 of 104 ± 3 kcal. This can be compared with $DH^\circ(RO\text{-}H)$ of 104 kcal in all the aliphatic alcohols and 106 kcal for $DH^\circ(RCO_2\text{-}H)$. Assuming that the second O-H bond dissociation energy in H_2SO_4

is not affected by removing the first, then $\Delta H^\circ_f(SO_4) = -73 \pm 4$ can be calculated for the SO_4 biradical. This has some very interesting consequences which will be pursued later in the discussion of the kinetics of SO_2 oxidation. For the moment simply note that SO_4 is a stable biradical with an O_3S-O bond dissociation energy = 28 ± 4. At 25°C SO_4 would be expected to be a long-lived species. It has a more stable cyclic analogue $O_2\overline{S\text{-}O\text{-}O}$ whose ΔH°_{f298} can be estimated from known groups and an assigned strain energy of 18 ± 2 kcal as -77 ± 2. Whereas SO_4 biradical can be triplet or singlet, the cyclic three-membered ring isomer can only be singlet.

Using an assumption that has been very successful in treating organic hydroperoxides ROOH, namely that the O-H bond dissociation energy is the same as in H_2O_2, namely 90 ± 1 kcal, then it can be estimated that $\Delta H^\circ_{f298}[HO(SO_2)OO^\cdot]_{gas} = -114 \pm 4$ kcal and that this radical is stable relative to dissociation into $HOSO_2^\cdot$ radical + O_2 by only 16 ± 5 kcal. This implies that this radical is probably a very important intermediate in photochemical smog involving sulfur-containing species.

Bond dissociation energies for the double bonded O atoms in sulfone derivatives are tabulated in Table 12. They seem surprisingly insensitive to the substituents on the central group with the exceptions of Cl_2SO_2 and SO_3. All of the other values can be approximated as 111 ± 2 kcal. The exceptional stability of SF_6 is indicated by the high value of 146 ± 5 for removing two F atoms.

Comparing these $R_2SO{=}O$ bond dissociation energies with the values for $R_2S{=}O$ (Table 9) reveals that they are uniformly less by about 8 kcal for electronegative R. Even for the $SO_2Cl_2/SOCl_2$ pair, this relation holds. This is not the case for the alkyl sulfones where the $DH^\circ(R_2S{=}O)$ values are uniformly less by about 23 kcal than $DH^\circ(R_2SO{=}O)$. One consequence of these relations is that the four valence states of sulfur will be unstable with respect to disporportionation when the ligands to S are alkyl or aryl groups, while the opposite will be true for electronegative groups. As examples of this tendency

$$2\ \phi SO\phi \rightleftarrows \phi S\phi + \phi SO_2\phi + 24 \text{ kcal}$$

$$2\ CH_3SOCH_3 \rightleftarrows CH_3SCH_3 + CH_3SO_2CH_3 + 26 \text{ kcal}$$

$$2F_2SO \rightleftharpoons SF_2 + SO_2F_2 \quad -7 \text{ kcal}$$

$$2Cl_2SO \rightleftharpoons SCl_2 + SO_2Cl_2 \quad -10 \text{ kcal}$$

Kice (37) has noted the "bond-weakening effect" of SO on adjacent bonds ascribing the effect to the stability of the SO radicals. From the above as well as from data to be presented on bond strengths, it can be concluded that the instability actually arises from the ΔH°_f of the parent molecule; for the sulfones and sulfoxides the principle of alternating polarity (26, 29), which is so important in determining thermochemical stability is illustrated again. It has already been noted that the ϕSO radical has less stabilization energy than ϕS or ϕSO_2.

Very few direct measurements of single bond dissociation energies for hexavalent sulfur compounds have been made. Mackle and colleagues (47) used toluene carrier techniques to measure the rates of pyrolysis of alkyl and aryl sulfones. However, their assignments of Arrhenius parameters were inconsistent and usually too low. Reinterpretation and scaling of their Arrhenius parameters using presently available thermochemical data lead to the bond dissociation energies shown in Table 12.

TABLE 12. S=O BOND DISSOCIATION ENERGIES IN HEXAVALENT SULFUR SPECIES

Species	Bond Dissociation Energy	Species	Bond Dissociation Energy
$O_2S = O$	83.3	$Me_2SO = O$	112
$F_2SO = O$	110 ± 5	$Et_2SO = O$	112
$Cl_2SO = O$	95	$\phi_2SO = O$	113
$(HO)_2SO = O$	110 ± 3	$\phi SO{=}O$	109
$(MeO)_2SO = O$	108	$(\phi SO_2)\phi SO{=}O$	122
$(EtO)_2SO = O$	109	$(\phi SO)\phi SO{=}O$	122 ± 3
$[F_4S = F_2$	146 ± 5]	$(\phi S)\phi SO{=}O$	115 ± 4
$SF_4 = O$	102 ± 6		

The data on the alkyl sulfones are self-consistent within ± 2 kcal, which is about the reliability of the ΔH°_f data. From complex kinetic studies of the radiolysis of CH_3SO_2Cl in cyclohexane, Horowitz (48) has evaluated Keq for

$$MeSO_2 \underset{\leftarrow}{\overset{1}{\rightleftharpoons}} Me + SO_2$$

in the range 60°-122°C; from its temperature coefficient the values ΔH°_1 = 15.6 kcal/mole and ΔS°_c = 23 e.u. were derived. In the gas phase ΔS°_p = 35 e.u., so an estimated ΔH° = 17.2 kcal/mole would be the appropriate value for the gas phase dissociation, in excellent agreement with the data in Table 13.

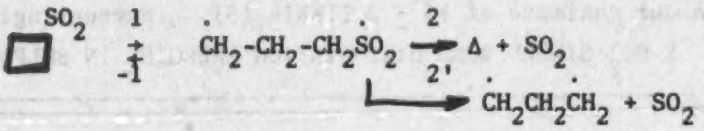
Further corroborating evidence for both of these bond dissociation energies comes from the work of Good and Thynne (49) who measured the direct gas phase equilibrium between CH_3 + SO_2. They found ΔH_1 = 20 ± 2, while values for the equilibrium $C_2H_5 + SO_2 \rightleftharpoons C_2H_5SO_2$ gave ΔH_1 = -17 ± 1 kcal/mole, in excellent agreement with our estimate of 16 ± 2 (Table 13). Interestingly, they claimed

TABLE 13. X-SO_2 SINGLE BOND DISSOCIATION ENERGIES IN SULFONE DERIVATIVES

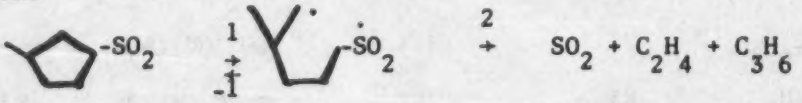
Species	Bond Dissociation Energy	$D_1 + D_2$	Species	Bond Dissociation Energy	$D_1 + D_2$
$CH_3(SO_2)$-CH_3	68	86	SO_2F_2	[100]	148
$Et(SO_2)$-C_2H_5	68	84	SO_2Cl_2	[63]	75
$CH_3(SO_2)$-allyl	55	73	$SO_2(OH)_2$	[88]	125
$CH_3(SO_2)$-benzyl	56	74	$SO_2(F)(OH)$		136
$C_6H_5(SO_2)C_6H_5$	70	114	$SO_2(HO)(O_2H)$		95
$CH_3(SO_2)C_6H_5$	83	101	$F(SF_4)F$	93 ± 3	147]
$C_6H_5(SO_2)CH_3$	54	101		79 (Ref. 50)	147 ± 3 (Ref. 50)
$C_6H_5SO_2$-$SO_2C_6H_5$	41 ± 1				
$C_6H_5SO_2$-SOC_6H_5	28 ± 1				

to observe activation energies of about 3 kcal/mole for both of these addition reactions and found them very much slower than the same radical reactions with O_2. This would tend to support the analogy between CO (or CO_2) and SO_2. CO has an appreciable reorganization energy of about 75 kcal and shows a small activation energy for radical or atom addition which varies with the electronegativity of the radical.

Cornell and Tsang (51) have conducted toluene carrier studies of the pyrolysis of trimethylene sulfone and 2-methyl sulfolane. Very interestingly, for the former they find only cyclopropane and only traces of propylene, suggesting that trimethylene is not an intermediate. The high A-factor of $10^{16.1}$ sec^{-1} and E_{act} = 56 ± 1 kcal suggest an open ring, very loose transition state. Assuming 19 kcal strain energy for the ring, an estimated 49 kcal would be required for the ΔH of ring opening to form the biradical:



If reaction 2, which is 38 kcal exothermic, has a loose transition state for the S_{n2} displacement of SO_2 from C by the free radical end and an activation energy of 7 kcal, this would be compatible with the observations. The competing reaction 2' to form trimethylene + SO_2 with a 16 kcal activation energy and a higher A-factor would still be about tenfold slower than reaction 2, which is in agreement with the very small amount of propylene found. Their study of 3-methyl sulfolane



yields again a high A-factor suggestive of a loose transition state and an activation energy of 66.4 kcal. This would suggest an estimated value for $\Delta H_1 \simeq 63 \pm 2$ kcal, which suggests that step 1 is rate determining with subsequent steps having an activation energy not exceeding 8-11 kcal and a high A-factor on the assumption that $E_{-1} \simeq 3$ kcal with an expectedly low A-factor of about 10^{12} sec^{-1}. Since the energy to detach SO_2 from the biradical requires approximately 15 kcal, this is a barely possible intermediate step. It is not

unlikely that the biradical cleaves into the three final species with an activation energy appreciably lower than this. Alternatively, a displacement reaction similar to that observed for the trimethylene sulfone might be expected. Its parameters are in the range of interest and would lead to methyl cyclobutane as a metastable intermediate which decomposes about threefold faster than the sulfone. The authors actually found a C_5 product, which they could not identify and which amounted to about 10% of the decomposition, could well be the cyclobutane derivative.

On this basis are derived the values for D_1 for the sulfones shown in Table 13. If D_1-D_2 is considered for the symmetrical sulfones, it has the value 50 $\pm$ 2 kcal, which can be considered a reorganization energy of the SO_2 group. While there is no reason to expect this to be a constant independent of R in R_2SO_2, note that it is consistent with one of the few directly measured values of F-SO_2F from shock tube studies (52). The authors fitted their data using RRK theory to bond strengths of 81 and 95 kcal/mole. They chose the former as giving a better fit to their data. However, the number of degrees of freedom and their A-factor were unjustifiably small. More acceptable values for the latter yield higher values for E_o closer to 100 kcal when extrapolated back to room temperature.

This latter value gives D_1-D_2 = 52 $\pm$ 2 kcal, which is in good agreement with the other sulfones. Assuming that this difference applies to Cl_2SO_2, it can be estimated that DH°(ClSO$_2$-Cl) = 63 as shown in Table 13. In similar fashion reanalysis of the shock tube data on SF_6 leads to a F_5S-F bond dissociation energy at room temperature of 93 kcal (53), which is also compatible with electron impact and electron affinity data on SF_6 and SF_5(54). This differs appreciably from the values selected by Hildenbrand (50), so the subject deserves further study. Note, however, that it yields D_1-D_2 = 39 for the SF_4 series.

Assignment of the constant difference for SO_2R_2, D_1-D_2 = 50 $\pm$ 2 yields the bond strengths DH°(HOSO$_2$-OH) = 88 kcal shown in Table 2 and ΔH°_f(SO_2OH) = -98 kcal.

The ΔH°_f deduced for the substituted SO_3 radicals permit us to draw some conclusions concerning SO_3. From the data in Table 11 it can be estimated that DH°(F-SO_2O$^\cdot$) = 51 $\pm$ 1.5 kcal and DH°(HO-SO_2O$^\cdot$) = 39 $\pm$ 2 kcal. From ΔH°_f

($HOSO_2$) = -98 ± 3 can be calculated an H-O bond dissociation energy of 81 kcal for the first bond in H_2SO_3 and a value of 55 kcal for $DH^\circ[H\text{-}OSO_2]$. This gives 26 kcal as the reorganization energy of the isomeric SO_3 biradical $O\text{-}SO\text{-}O$ to SO_3. This permits a calculation of the R-O bond dissociation energies in the sulfites $(RO)_2SO$. The data in Table 13 reveals 89 kcal for $D_1 + D_2$ for $CH_3\text{-}OSO_2CH_3$; using $D_1\text{-}D_2$ = 26 kcal to estimate, D_1 = 57.5 kcal and D_2 = 31.5 kcal. DH° ($HO\text{-}SO_2$) = 36 kcal, which is only slightly weaker than the attachment of the OH bond to SO_3.

In H_2SO_5 the O-O bond strength can be estimated to be 36 kcal, appreciably stronger than the 22 kcal estimated for the O-O bond in $H_2S_2O_8$ but typical of the differences in O-O bond strengths between peroxides and hydroperoxides. While $\Delta H^\circ_f[HO(SO)O_2H]_{gas}$ is not known, upper and lower limits can be estimated for it from ΔH°_f of the sulfur analogue $HO(SO_2)O_2H$ and the >S=O bond dissociation values listed in Table 12. For polar species OH, OR, and F, or even alkyl and aryl substituents, this bond is 111 ± 2 kcal. For O substituent it is 15 kcal lower. With one OH and one OOH substituent, an estimate would be that 107 ± 4 may well bracket all likely values and thus give $\Delta H^\circ_f(HO(SO)O_2H)_{gas}$ = 105 ± 5 kcal. This would make the O-O bond dissociation energy in this compound only 16 ± 6 kcal, from which it can be concluded that the acid is unstable at temperatures above 200°K. This is the weakest of O-O bonds in the entire sequence.

An interesting bond strength is the central O-S bond in pyrosulfuric acid $HOSO_2\text{-}O\text{-}SO_2OH$. For this bond an estimate would be that $DH^\circ(HOSO_2\text{-}OSO_3H)$ = 59 ± 5 kcal, which explains why the various polymeric forms of SO_3 are quite stable in the absence of an acid or base catalyst.

The observation (37,4Z) that the $\phi SO_2\text{-}SO_2\phi$ bond fission has an activation energy of 41 kcal in inert solvents permits us to estimate ΔH°_f ($\phi SO_2^\cdot$) (Table 13) and a stabilization energy in $\phi CH_2^\cdot$ of 13 kcal. The stabilization observed in $\phi S^\cdot$ is some 4.5 kcal less than that in ϕSO_2, and this is probably to be expected since the source of the stability is the donation of charge from ϕ to the SO_2 group, and the latter is much more electrophilic than S.

For dithionic acid $H_2S_2O_6$ where ΔH°_f is known only approximately, it can be estimated that $DH^\circ(HOSO_2\text{-}SO_2OH)$ = 50 ± 10 kcal. It would be anticipated from the analogy with $(\phi SO_2)_2$ that a more negative ΔH°_f and a stronger bond closer to

60 kcal would be more likely.

One of the more interesting compounds of sulfur is the SO_4 discussed earier. The cyclic form is stable relative to the decomposition into $SO_2 + O_2$ by about 5 ± 3 kcal but might have a high activation energy for such a decomposition because of spin forbiddeness. It is marginally more stable than the biradical SO_4 by about 3 ± 5 kcal. The SO_4 birdadical is stable realtive to decomposition into $SO_3 + O$ by 38 kcal and also stable relative to decomposition into $SO_2 + O_2$ by 2 ± 5 kcal. If SO_4 is a stable or metastable species, however, this latter mode of decomposition is probably restrained by dynamic considerations rather than energetic ones.

There is good experimental evidence for believing that SO_4 biradical is a stable species in the gas phase. Westenberg and deHass (55) have shown that at room temperature O atoms and SO_3 added together in a very rapid thermolecular reaction with rate constants that can be rationalized only by assuming a reasonably deep well for the reaction with no activation barrier. A 38 kcal O_3-S-O bond would fulfill this requirement. The fate of SO_4 is somewhat mysterious in this system as it does not lead to $SO_2 + O_2$. In fact, at much higher temperatures $O + SO_3 \rightarrow SO_2 + O_2$ appears to be a slow reaction (56,57) with appreciable activation energy. One would expect from its manner of formation from $O + SO_3$ that the stable form of biradical SO_4 would be the triplet state and that this could account for its dynamic stability relative to cyclic peroxy-SO_4.

One fate that could be anticipated for radical SO_4 is self polymerization to $(SO_4)_n$, either linear or cyclic, or polymerization with SO_3 to form linear or cyclic $(SO_3)_n SO_4$ with a peroxide linkage. The polymer $(SO_4)_n$ could be looked upon as a copolymer of SO_2 and O_2, and an estimate of its ΔH^o_f extrapolated from known groups is -95 kcal/mole SO_4. Thus it would be stable by about 24 kcal/mole against decomposition into $SO_2 + O_2$, and it would be thermoneutral with respect to the depolymerization into $SO_3 + 1/2\ O_2$. The O-O bond in such a polymer is estimated to be 22 kcal/mole, like that in $H_2S_2O_8$ so it could unzip at about room temperature.

The copolymer with SO_3 is expected to be more stable with an 11 kcal bond energy for the process

$$SO_4 + SO_3 \rightleftarrows \dot{O}(SO_2)O(SO_2)\dot{O}$$

While this is not enough to render the gas phase dimer stable at 300° K, it could readily stabilize by sorbing on glass surfaces, or by forming there in a heterogeneous reaction.

It has been reported (58) that when an electric discharge is passed through a SO_2/O_2 mixture at 0.5 torr ($O_2 >> SO_2$) a white solid can be condensed with formula SO_4 and a melting point of +3° C. On melting it evolves O_2 and leaves a liquid residue with the composition S_2O_7. These substances could well be the polymers discussed above which would be more stable in condensed states.

SECTION 5

OXIDATION OF SULFUR-CONTAINING MOLECULES

The kinetics of oxidation of sulfur compounds may be divided into two categories; the oxidation at low temperatures (~25°C), which is of interest in photochemical smog formation and stratospheric chemistry, and the high temperature oxidation, which is of interest in fossil fuel burning plants and smelters. There has been at least one very recent review in each of these two regimes which summarizes current thinking and evidence on reaction steps, so there is no need to repeat the discussions to be found there (2,59). There is in addition a recent critical update of some of the elementary gas phase reaction rate constants involving simple S-containing radicals with O, H, and other simple molecules and radicals in flames (60). An additional article of interest in examining low temperature oxidation processes and their relation to aerosol formation has also appeared recently (61). The discussion here will be confined to considering some of the critical elementary steps in these oxidation schemes, starting with the low temperature photochemical system.

Photochemical smog formation refers to the oxidation of hydrocarbons present in ambient atmosphere at low concentration (1-10 ppm) triggered by photochemical (sunlight) decomposition of NO_2 also present in low concentrations (0.1-2.0 ppm). The process is accompanied by a catalytic production of O_3 (0.1 to 0.5 ppm maximum) and other oxidized species and usually aerosols.

Although photolysis produces O atoms from both NO_2 and O_3, these are rapidly scavenged by O_2 molecules in a process that achieves a very low photostationary concentration dominated by:

$$NO_2 + h\nu \ (\lambda < 4100\text{Å}) \xrightarrow{1} NO + O$$

$$O + O_2 + M \xrightarrow{2} O_3 + M$$

$$NO + O_3 \xrightarrow{3} NO_2 + O_2$$

$$(O)_{ss} = \frac{k_1(I_o \bar{\epsilon} NO_2)\ (NO_2)}{k_2(O_2)(M)}$$

where I_o is the flux of radiation and $\bar{\epsilon} NO_2$ is the weighted extinction coefficient of NO_2. Because of the low concentrations achieved, reactions of O atoms with ambient molecules will not be of interest unless their bimolecular rate constants exceed 10^8 ℓ/mole-sec. Instead it appears that other radicals such as OH, HO_2, and RO_2, which react only very slowly or not at all with O_2, will dominate the reaction chemistry. Saturated hydrocarbons, for example, appear only to be attacked at significant rates by OH radicals.

The most important sulfur-containing species in ambient atmosphere is SO_2, and secondarily, SO_3. Both of these react with O atoms at rates whose apparent bimolecular rate constants of about 10^8 ℓ/mole-sec (55,60) are close to the minimum rate considered significant. In very bright sunlight at higher NO_2 concentrations, these reactions may be important, but not otherwise.

The reaction of OH with both SO_2 and SO_3 is expected to be extremely rapid with rate constants approaching 10^{11} and 10^{12} $ℓ^2/mole^2$-sec:

$$OH + SO_2 + M \rightarrow HOSO_2 + M$$

$$OH + SO_3 + M \rightarrow HOSO_3 + M$$

The resulting radicals have $DH^\circ(HO\text{-}SO_2) = 36 \pm 3$ kcal and $DH^\circ(HO\text{-}SO_3) = 39 \pm 2$ kcal and thus are expected to be quite stable with respect to dissociation. The addition reactions are expected to have negative temperature coefficients.

The HSO_4 radical can form a very strong OH bond (104 kcal) and is expected to be more active than RO radicals in either adding to double bonds of olefins or in abstracting H atoms from hydrocarbons. It can also react with NO to form mononitrosyl sulfuric acid $HO(SO_2)ONO$ with $DH^\circ(HOSO_2O\text{-}NO) = 22 \pm 2$ kcal and $DH^\circ(HOSO_2\text{-}ONO) = 35 \pm 2$ kcal. This addition reaction is expected to have very little or zero activation energy. The nitrosyl sulfuric acid has a very large heat of condensation and will be readily sorbed on surfaces and exothermically hydrolyzed to sulfuric plus nitrous acids. It should also form metastable

complexes with H_2O in the gas phase if the humidity is high enough.

HSO_4 will also react rapidly with NO_2 at almost every collision ($k \sim 10^{10}$ ℓ/mole-sec) to form nitryl sulfuric acid $HO(SO_2)ONO_2$. This species has an estimated $\Delta H^\circ_{f298} = -139 \pm 3$ kcal and about the same bond energy for redissociation as the nitrosyl ester, namely 22 ± 2 kcal. It will also form complexes with H_2O in the gas phase and hydrolyze readily on surfaces to $H_2SO_4 + HNO_3$.

Nitryl and nitrosyl sulfuric acid have relatively week O-N bonds as estimated and at STP will have half-lives of about 1-10 seconds. At lower temperatures typical of the stratosphere (220°K), thermal dissociation is negligible, while on hot, smoggy days, redissociation is very fast.

It has been suggested that HSO_4 can react with O_2 to form the peroxy radical $HO(SO_2)O_3\cdot$, which can then go on to react with NO to form NO_2 and HSO_5 (62). Starting with the estimated $\Delta H^\circ_f[HO(SO_2)O_3H] = -152 \pm 2$, it can be estimated using group additivity rules for polyoxy compounds that $\Delta H^\circ_f[HO(SO_2)O_3H] = -133 \pm 3$ kcal and $H_f[HO(SO_2)O_4H] = -114 \pm 3$ kcal. In such polyoxides the $RO_{n+1}-H_2$ bond strength appears to be 90 ± 1 kcal as in H_2O_2, so that the estimate $\Delta H^\circ_f[HO(SO_2)O_3\cdot] = -95 \pm 3$ kcal can be made. Thus the addition of O_2 to HSO_4 is endothermic by 20 ± 3.5 kcal, and $HSO_6\cdot$ is not expected to exist. In contrast, the radical $HOSO_2$ can form a bond with O_2 with a dissociation energy of about 16 ± 5 kcal, hence the radical HSO_5 is expected to be a significant species in smoggy atmospheres containing SO_2. $DH^\circ(HOSO_3\text{-}O)$ is estimated to be 48 ± 5 kcal, so that this radical should be capable of oxidizing NO to NO_2. Note that the adduct with NO or NO_2 will not be stable. The reaction $HSO_5 + NO_2 \rightleftarrows NO_3 + HSO_4$ is estimated to have $\Delta H^\circ = 0 \pm 4$ kcal.

If we employ our rule that the reorganization of SO_2 is 51 kcal, then $\Delta H^\circ_f(HO_2\text{-}SO_2) = -73 \pm 4$ kcal can be calculated. This suggests that the radicals HO_2 and RO_2 may react with SO_2 to form SO_3 + HO and RO, respectively, with little or no activation energy. Thus SO_2 can, like NO, act as a catalyst for the conversion of realtively inert peroxy radicals into more active oxy radicals:

$$SO_2 + RO_2 \rightarrow SO_3 + RO$$

The intermediate adduct, RO_2SO_2 has a relatively weak $RO\text{-}OSO_2$ bond, 4 ± 4 kcal, and will not be stable.

The HSO_3 radical has a fairly strong HSO_2-O bond, estimated at about 97 ± 4 kcal, hence it will not oxidize NO_2, NO, or SO_2. According to calculations, it will not have an affinity for NO. However, it should react readily with NO_2 to form the fairly stable nitrosyl sulfuric acid:

$$NO_2 + HSO_3 \rightarrow HO(-SO_2-)ONO + 37 \pm 5 \text{ kcal}$$

As we have noted this will have a relatively short half-life at 300°K to dissociate into HSO_4 + NO or to hydrolyze.

The oxidation of sulfur compounds in flames and at high temperatures involves all possible valence states. Hence, isomeric forms of these species, particularly as radicals, become of interest. A very important reaction involves the interactions of H atoms with SO_2 and SO_3. $DH^\circ(SO_3\text{-}H) = 55 \pm 3$ kcal so that one expects H atoms to add very rapidly to SO_3. In high temperature regimes the adduct is expected to have a very short life time for redissociation into SO_2 + OH for which $DH^\circ = 36$, so that the reaction

$$H + SO_3 \rightleftarrows HOSO_2^* \rightarrow HO + SO_2$$

is expected to proceed very rapidly with little or no activation energy. The reactions of H atoms with SO_2 are probably more interesting in most flame systems. These reactions are complicated by the existence of isomeric forms of radicals and molecules. The compound H_2SO_2 has three isomeric forms: $(HO)_2$-S, HSO(OH), and H_2SO_2. For these forms we have estimated ΔH°_f of -67 ± 5, -72 ± 5, and -64 ± 4, respectively. The radical HSO_2 has two isomeric forms, H-SO_2 and HO-S=O, for which by our various rules we can deduce ΔH°_f of -42 ±4 and -60 ± 3 kcal, respectively. Thus the latter will be significantly more stable with an H-OSO bond dissociation energy of 41 kcal. Efforts to measure the rate of addition of H atoms to SO_2 in flow systems have been made difficult by the very rapid wall recombination (63). However, flame studies which have been recently reviewed (60) indicate a fairly rapid three-body reversible recombination above 1600°K. This would be compatible with the 41 kcal bond energy.

Sulfur compounds in the divalent state will be expected to react very rapidly with O atoms to form sulfoxides:

$$R_2S + O \rightarrow R_2SO$$

This reaction is very exothermic (Table 9) and in the gas phase can be followed by dissociation of the weaker R-S bond. Slagle and co-workers (64) have shown that these reactions at room temperatures proceed with zero activation energy for RSH and R_2S and have suggested that with H_2S the excited adduct H_2SO^* can rearrange to give the isomeric $HOSH^*$, which is estimated to be about 20 $\pm$ 5 kcal more stable. With the internal energies available in these adducts, this seems entirely reasonable.

One of the other high temperature reactions which has excited some interest is the bimolecular reaction between NO_2 and SO_2:

$$NO_2 + SO_2 \rightarrow \quad NO\text{-}SO_3 + 11 \text{ kcal}$$

Despite its exothermicity this reaction appears to have a surprisingly high activation energy of the order of 26 kcal (65). Rate studies on this system have proven difficult because the bimolecular reaction of $2NO_2 \rightarrow 2NO + O_2$ is faster than the competing reactions. In examining this reaction note that the transition state must be close in structure to the radical species:

$$O - N - O - SO_2$$

We can estimate the ΔH°_f for this species by observing that ΔH°_f ($ONOSO_3H$) = -125 $\pm$ 3 kcal. If the S-OH bond dissociation energy in this anhydride is the same as its value in H_2SO_4 (Table 9), then $\Delta H^\circ_f(ONO\text{-}SO_2)$ = -46 $\pm$ 4 kcal can be calculated. Thus the radical lies above $SO_2 + NO_2$ by 17 $\pm$ 4 kcal, and this would be a minimum activation energy for the reaction. On this basis the transition state for the reaction lies between the free molecules and the above radical with an intrinsic energy only 9 kcal above the radical. This 9 kcal would be a reasonable intrinsic activation energy for an atom transfer reaction. A similar situation occurs in the reaction of NO_2 with CO, which is exothermic to form $NO + CO_2$ by 54 kcal, but has an activation energy of 27 kcal. By similar methods ΔH°_f (ONOCO) = 1 $\pm$ 3 kcal can be estimated, so that the radical lies 19.5 $\pm$ 3 kcal above NO_2 + CO in ΔH°_f, and the transfer reaction has an intrinsic activation energy of only 8 kcal.

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APPENDIX

METHOD OF ESTIMATION OF ΔH°_f OF ACID ANHYDRIDES

To estimate the ΔH°_f of the various sulfur and nitrogen oxy-acid anhydrides, analogies have been used which represent a correction to the rules of bond additivity. Data exist for a number of acid anhydrides and for the corresponding acids. These are summarized in Table A-1 where we list in addition data on the heats of hydrolysis of these anhydrides in the ideal gas state. The listings are roughly in order of exothermicity and range from ΔH = -14 to +6.0 kcal. The range is not random but appears to be correlated with the acidity (pKa) of the two acids involved. Thus anhydrides of acids whose pKa $\lesssim$ 5 seem to hydrolyze with $\Delta H_{hyd} \approx -10 \pm 2$ kcal. As the pKa of one or more of the acids decreases, this changes to positive. Anhydrides of MeOH, for example, seem to have $\Delta H_{hyd} \approx 5 \pm 2$ kcal.

On the basis of the above correlations, it would be expected that anhydrides of nitric, sulfuric, and acetic in any combination would have $\Delta H_{hyd} = -12 \pm 2$ kcal. And on this basis it could be estimated:

$$\Delta H^{\circ}_f\ [HO(SO_2)O\ COCH_3] = -212 \pm 2$$

$$\Delta H^{\circ}_f\ [HO(SO_2)\ ONO_2] = -139 \pm 2$$

$$\Delta H^{\circ}_f\ [CH_3(CO)ONO_2] = -65 \pm 2$$

On the same basis it could be estimated:

$$\Delta H^{\circ}_f [O_2N\text{-}NH_2] = 15 \pm 2$$

$$\Delta H^{\circ}_f [HO(SO_2)NH_2] = -124 \pm 2$$

For HONO the anhydride ΔH°_f can be bracheted between that of stable N_2O (+19.8 kcal) and separated NO + NO_2 (+29.4 kcal). A reasonable choice would be $\Delta H^{\circ}_f[(ON)_2O) = 24 \pm 2$ kcal. Bond additivity would then yield ΔH°_f $(ONONO_2)$ =

13.5 ± 1 kcal which can be compared to 2.5 kcal for the stable forms of N_2O_4. ΔH°_{hyd} [$(ON(_2O]$ is then -2.5 kcal, while ΔH_{hyd} [$ONONO_2$] = -6 kcal, both of which seem quite reasonable. On this basis, guided by the pKa considerations, it can be estimated.

$$\Delta H^\circ_f[HO(SO_2)ONO] = -129 \pm 2 \text{ kcal}$$

$$\Delta H^\circ_f[CH_3(CO)ONO] = -56 \pm 2 \text{ kcal}$$

TABLE A-1. ΔH^{o}_{f} FOR SOME ACID ANHYDRIDES AND THEIR HEATS OF HYDROLYSIS IN THE IDEAL GAS STATE

Ref.	Anhydride	ΔH^{o}_{f}	ΔH^{o}_{hyd}
4	$(CH_3CO)_2O$	-137.1	-11.7
6	$(NO_2)_2O$	2.7	- 9.1
(Table 11)	$(HOSO_2)_2O$	-282 ± 3	-14 ± 3
7	Cl_2O	21.0	- 7 ± 5
(Table 11)	$HOSO_2F$	-180	-4
(Table 11)	$HOSO_2Cl$	-133	-8
(4)	CH_3COF	-104	-6
(4)	CH_3COCl	-58.9	-8.5
(4)	CH_3COBr	-45.6	-8.6
(4)	CH_3COI	-30.3	-8.9
(Table 11)	SO_2F_2	-181 ± 2	-5.7 ± 2
(Table 11)	SO_2Cl_2	-84.8	-12.4
Table 2	HCOSH	-30	-7.5 ± 1
4	$HCONH_2$	-44.5	1 ± 2
4	O_2NOMe	-28.6	6.4
4	ONOMe	-15.6	7.1
22	CH_3COOMe	-98.0	4.5
4	Me_2O	-44.0	6.0
46	HOOOH	-13	7.0
Table 11	$HOSO_2(OMe)$	-170.5 ± 2	4.0